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APPLICATION OF ELECTROSTATIC MODEL OF HYDROGEN BOND TO HYDROGEN BONDING IN SOME ALIPHATIC ALCOHOLS AND PHENOL COMPOUNDS IN SOLUTIONS OF POLAR SOLVENTS

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ABSTRACT.. Coggeshall's method of treatment of electrostatic model of hydrogen bond as developed in an earlier paper (Kastha and Medhi, 1960) for investigating hydrogen bonding in aniline and substituted anilines in solutions in polar solvents, has been applied to the case where such hydrogen bridges are formed in very dilute solution between the solute molecules of some aliphatic alcohols, phenol and substituted phenols and the solvent molecules of ether, tetrahydrofuran and pyridine. The validity of the method has been discussed and it has been concluded that the method may be used to explain qualitatively certain features of hydrogen bonding in such cases.

INTRODUCTION

Recently, Kastha and Medhi (1963) have applied Coggeshall's method of treatment of the electrostatic model of hydrogen bond to the case of hydrogen bonding in aniline and substituted anilines in different environments and have, under certain simplifying assumptions, been able to explain qualitatively certain experimental results previously obtained by them (Medhi and Kastha, 1963). It has been found, on the basis of this model, that in the series of phenyl amines investigated, the ratio of the values of the total solvent shifts in the frequencies of symmetric and asymmetric N–H stretching vibrations in the NH_2 group in the molecule of any of the compounds in solutions in two polar solvents is a constant for the pair of solvents and is almost independent of the nature of the compound. However, in this case the investigation was limited to hydrogen bonds involving N–H bonds. In order to see whether such a model of hydrogen bond is also applicable when the hydrogen bridges are formed in solution between the hydrogen atom in the molecule of compounds containing other type of X–H bonds and molecules of polar solvents, the investigation has been extended to the case of solutions in polar solvents of compounds whose molecules contain hydroxyl groups.

Application of Coggeshall's model to O–H...X hydrogen bonds

Following Coggeshall (1950) and the method of application of his model as developed in a previous paper (Kastha and Medhi, 1963) it is easily found that the ratio of the values of the solvent shifts ($\Delta\nu$) in the frequency of O–H stretching vibration in the molecule of a certain compound due to formation of linear O–H...X bridge in very dilute solutions of the compound in two polar solvents whose molecules contain atoms $\mathbf{X}_1$ and $\mathbf{X}_2$ respectively is given by

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \left(\frac{q_{X_1}}{q_{X_2}} \cdot \frac{R_{H...X_2}}{R_{H...X_1}}\right)^2 \qquad \ldots (1)$$

where q_{X_1} and q_{X_2} are the unbalanced charges on atoms X_1 and X_2 respectively and $R_{H...X_1}$ and $R_{H...X_2}$ respectively denote the distances between the hydrogen atom in the O–H bond in a molecule of the compound used as the solute and the atoms X_1 and X_2 of the two polar solvent molecules forming the hydrogen bridges O–H...X_1 and O–H...X_2 respectively. It is seen from equation (1) that the ratio $\Delta\nu_1/\Delta\nu_2$ should be approximately a constant for a particular pair of solvents and be almost independent of the nature of the compound containing the hydroxyl group. This would strictly hold in the case of structurally similar compounds provided that the distribution of unbalanced charges on the atoms of the solvent molecules taking part in the formation of hydrogen bridges is not affected to a

TABLE I

Compound	$\frac{\Delta\nu \text{ tetrahydrofuran}}{\Delta\nu \text{ ether}}$	$\frac{\Delta\nu \text{ pyridine}}{\Delta\nu \text{ ether}}$
Isopropyl alcohol	1.17	1.99
Tertiarybutyl alcohol	1.12	1.96
Ethyl alcohol	1.11	1.96
Methyl alcohol	1.10	2.01
Propargyl alcohol	1.08	1.98
Phenol	0.99	1.70
p-Cresol	1.04	1.77
m-Cresol	1.44	1.73
p-Chlorophenol	1.05	..
p-Nitrophenol	1.05	..
m-Nitrophenol	1.04	..

significant extent by the charges on the atoms of the solute molecules. Moreover, if X_1 and X_2 represent the same atom, $q_{x_1} \approx q_{x_2}$ and $R_{H\ldots X_1} \approx R_{\ldots HX_2}$ we have from Eqn. (1) $\Delta\nu_1/\Delta\nu_2 \approx 1$. In order to verify how far such conclusions are true, the values of the ratio of the solvent shifts ($\Delta\nu_1/\Delta\nu_2$) in the vibrational frequency of the hydroxyl group in the molecules of compounds, calculated from the results reported by Henry (1959) in the case of very dilute solutions of some aliphatic alcohols, phenol and substituted phenols in ether, tetrahydrofuran and pyridine, are given in Table I

DISCUSSION

It is seen from Table I that the values of $\Delta\nu_1/\Delta\nu_2$ for the pair of solvents, tetrahydrofuran and ether (for which X_1 and X_2 both represent atoms of oxygen) are almost constant and independent of the nature of the solute molecules even though the molecules of the two series of solute compounds of aliphatic alcohols and aromatic phenols are different. Also the values of $\Delta\nu_1/\Delta\nu_2$ are almost equal to unity in each case. In the case of the two solvents, pyridine and ether the ratio of the solvent shifts $\Delta\nu_1/\Delta\nu_2$ is constant for the series of aliphatic alcohols and for the phenols. However, in this case the two values are different. This may be due to the difference in the nature of the molecules of the two series of compounds. It would, therefore, be interesting to compare the values of the ratio $\Delta\nu_1/\Delta\nu_2$ in the case of two structurally similar type of molecules, viz., the phenols and the phenyl amines, in solutions in pyridine and in ether. If the geometry of the hydrogen bridges formed in the two cases of substituted benzenes in solutions in the same pair of polar solvents is not much different it is easily seen that

$$\frac{(\Delta\nu_1/\Delta\nu_2)_{amines}^{phenyl}}{(\Delta\nu_1/\Delta\nu_2)_{phenols}} = \left\{\left(\frac{R_{H\ldots X_2}}{R_{H\ldots X_1}}\right)_{amines}^{phenyl} \Big/ \left(\frac{R_{H\ldots X_2}}{R_{H\ldots X_1}}\right)_{phenols}\right\}^2 \quad \ldots \quad (2)$$

A rough estimate of the value of the above ratio may be obtained from the values of the various interatomic distances involved in the hydrogen bond in the case of the phenyl amines and the phenol compounds. If the N–H and O-H bond lengths are taken as 1.09 Å and 0.96 Å respectively, and the values of the interatomic distances N–H...N, N–H...O, O–H...N and O–H...O involved in the various hydrogen bridges, as given by Pimental (1960), are used we get, for phenyl amines $R_{H..N} \approx 2.01$ Å and $R_{H..O} \approx 1.95$ Å and for the phenol compounds, $R_{H..N} \approx 1.88$ Å and $R_{O..H} \approx 1.71$ Å. Substituting these values on the right hand side expression of equation (2), we obtain,

$$\left(\frac{\Delta\nu_{pyridine}}{\Delta\nu_{ether}}\right)_{amines}^{phenyl} \Big/ \left(\frac{\Delta\nu_{pyridine}}{\Delta\nu_{ether}}\right)_{phenols} = \left\{\left(\frac{R_{H..O}}{R_{\ldots\ldots}}\right)_{amines}^{phenyl} \Big/ \left(\frac{R_{H..O}}{R_{\ldots\ldots}}\right)_{phenols}\right\}^2$$

$$\approx 1.14$$

The experimental value for the left hand side expression of equation (2) obtained by substituting the average of $\Delta\nu_1/\Delta\nu_2$ for phenyl amines [taken from the results of Kastha and Medhi (1963)] and that for the phenol compounds [taken from Table I] in solutions in pyridine and in ether, is found to be 1.09 and this agrees fairly well with the calculated value 1.14.

From the foregoing discussions it is concluded that the simple electrostatic model of hydrogen bonds investigated by Coggeshall in the case of hydrogen bonding between similar molecules may also be applied under certain restrictions to the case of formation of hydrogen bridges in solution between two dissimilar molecules of solute and solvent.

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